

Simple Recipe for Implementing Computation of First-Order Relativistic Corrections to Electron Correlation Energies in Framework of Direct Perturbation Theory

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ABSTRACT

The computation of the relativistic correction to the first order in $1/c^2$, where c is the velocity of light, is implemented at the levels of coupled cluster and many-body perturbation theory. The relativistic correction is obtained by applying direct perturbation theory through the first order, and it is shown that its implementation is straightforward if analytical energy gradients of the methods under consideration are available. Preliminary results were obtained by a numerical procedure and are reported for some closed-shell atoms (He, Be, Ne, and Ar) and molecules (CuH and SiH₄). © 1997 by John Wiley & Sons, Inc.

Introduction

Several *ab initio* methods have been developed for the simultaneous computation of relativistic and electron correlation effects in many-electron, polyatomic systems. On the one hand there are quasirelativistic approaches that use computational methods and computer codes for

nonrelativistic electron correlation treatments with little or no modification. These approaches include the use of relativistic effective core potentials (RECP, see ref. 1), the first-order Cowan–Griffin (CG) perturbation theory² with the mass-velocity and Darwin operators (MVD), and methods based on the second-order Douglas–Kroll (“no-pair”) approximation³ as developed by Heß.⁴ On the other hand, fully relativistic electron correlation methods for molecules such as second-order many-body

perturbation theory [MBPT(2), see ref. 5) or the configuration interaction method (CI, see ref. 6) were developed based on four-component Dirac–Hartree–Fock (DHF) theory.

Based on an approach proposed by Sewell,⁷ a relativistic “direct” perturbation theory (DPT) was developed by Rutkowski,^{8–10} Kutzelnigg,¹¹ and Franke and Kutzelnigg¹² to expand the Dirac equation “directly” in orders of $1/c^2$. This DPT method was developed further in the framework of DHF theory by Franke¹³ and Kutzelnigg and coworkers.^{14–16} The zeroth order of the DPT-DHF expansion refers to nonrelativistic Hartree–Fock (HF) theory, and higher order DPT corrections were implemented and computed up to $O(c^{-6})$ in the energy for closed-shell atomic systems.^{16,17} For molecules a program was developed^{13,14} that computes the first-order energy [i.e., correct to $O(c^{-2})$] at the HF level.

In the present work we make the important observation that the first-order DPT belongs to the category of approaches for relativistic effects that can be implemented into computer codes for non-relativistic electron correlation methods with little or no modification, because it is very similar to the first-order MVD perturbation theory. First-order DPT was implemented for CI calculations on He-like atoms by Ottsofski¹⁷ and Ottsofski and Kutzelnigg¹⁸ and in the framework of density functional theory (DFT) by van Wüllen.¹⁹ In the present work, we propose a simple recipe for its implementation into electron correlation methods such as MBPT and coupled-cluster (CC) theory to make possible the application of first-order DPT in calculations on molecules at the correlated level. This recipe is also applicable to other methods, and we will discuss its meaning in the context of HF and DFT theory.

Preliminary results will be presented for the closed-shell atoms He, Be, Ne, and Ar, and molecules CuH and SiH₄. These results include results from fourth-order MBPT [MBPT(4)], CC theory with single and double substitutions (CCSD), as well as the same method with noniterative triples [CCSD(T)].

Direct Perturbation Theory

Consider the Dirac–Fock–Coulomb equation (in atomic units and with the rest energy subtracted

from the one-electron Dirac Hamiltonian)

$$\begin{pmatrix} V_N + J_{11} + J_{22} - K_{11} & c\boldsymbol{\sigma} \cdot \mathbf{p} - K_{12} \\ c\boldsymbol{\sigma} \cdot \mathbf{p} - K_{21} & -2c^2 + V_N + J_{11} + J_{22} - K_{22} \end{pmatrix} \times \begin{pmatrix} \varphi_p \\ \psi_p \end{pmatrix} = \varepsilon_p \begin{pmatrix} \varphi_p \\ \psi_p \end{pmatrix}. \quad (1)$$

The bispinors (four-component molecular orbitals) are assumed to be normalized, mutually orthogonal,

$$\langle \varphi_p | \varphi_q \rangle + \langle \psi_p | \psi_q \rangle = \delta_{pq}, \quad (2)$$

and the matrix elements of J and K are given by integrals over $1/r_{12}$ in Mulliken notation,

$$\begin{aligned} \langle \omega | J_{11} | \tau \rangle &= \sum_i (\varphi_i \varphi_i | \omega \tau), \\ \langle \omega | J_{22} | \tau \rangle &= \sum_i (\psi_i \psi_i | \omega \tau), \end{aligned} \quad (3)$$

$$\begin{aligned} \langle \omega | K_{11} | \tau \rangle &= \sum_i (\varphi_i \omega | \varphi_i \tau), \\ \langle \omega | K_{22} | \tau \rangle &= \sum_i (\psi_i \omega | \psi_i \tau), \end{aligned} \quad (4)$$

$$\begin{aligned} \langle \omega | K_{12} | \tau \rangle &= \sum_i (\varphi_i \omega | \psi_i \tau), \\ \langle \omega | K_{21} | \tau \rangle &= \sum_i (\psi_i \omega | \varphi_i \tau). \end{aligned} \quad (5)$$

The summation is over occupied (two-component) spinors, c is the velocity of light, \mathbf{p} is the operator of momentum, and the components of $\boldsymbol{\sigma}$ are the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (6)$$

and the nuclear potential is

$$V_N = - \sum_i \sum_A \frac{Z_A}{r_{iA}}. \quad (7)$$

r_{iA} is the distance between electron i and nucleus A of charge Z_A , and r_{ij} is the distance between two electrons.

The basic idea of DPT is to apply a change of the metric,

$$\begin{pmatrix} \varphi_p \\ \tilde{\psi}_p \end{pmatrix} = \begin{pmatrix} \varphi_p \\ c\psi_p \end{pmatrix}, \quad (8)$$

and expand the transformed Dirac–Fock–Coulomb equation in orders of $1/c^2$. The DPT expansion is described in great detail in ref. 15. In the following, however, we wish to treat the relativistic DPT correction to the first order in $1/c^2$ as a simple external perturbation of strength α to one- and two-electron integrals (analogous to a nuclear displacement) and employ the well-known machinery of analytical energy gradients to compute the first-order DPT correction to nonrelativistic HF, MBPT, and CC theory (or other). At the zeroth order, the DPT result is

$$\psi_p^{(0)} = \frac{1}{2c} \boldsymbol{\sigma} \cdot \mathbf{p} \varphi_p^{(0)} = \frac{1}{2c} \boldsymbol{\sigma} \cdot \mathbf{p} \sum_{\mu} c_{\mu p}^{(0)} \phi_{\mu}, \quad (9)$$

where $\varphi_p^{(0)}$ has been expanded in a basis of spinors $\{\phi_{\mu}\}$ [two-component atomic orbitals (AOs)], and at the HF level, the zeroth-order energy is

$$E_{\text{HF}}^{(0)} = \sum_{\mu, \nu} P_{\mu\nu}^{(0)} \left[h_{\mu\nu} + \frac{1}{2} \sum_{\kappa, \lambda} P_{\kappa\lambda}^{(0)} \langle \mu\kappa \| \nu\lambda \rangle \right], \quad (10)$$

where

$$h_{\mu\nu} = \left\langle \phi_{\mu} \left| V_N + \frac{p^2}{2} \right| \phi_{\nu} \right\rangle, \quad (11)$$

$$\langle \mu\kappa \| \nu\lambda \rangle = (\phi_{\mu} \phi_{\nu} | \phi_{\kappa} \phi_{\lambda}) - (\phi_{\mu} \phi_{\lambda} | \phi_{\kappa} \phi_{\nu}), \quad (12)$$

and

$$P_{\mu\nu}^{(0)} = \sum_i [c_{\mu i}^{(0)}]^* c_{\nu i}^{(0)}. \quad (13)$$

A consequence of eq. (9) is that the first-order change of one- and two-electron integrals with respect to a perturbation parameter α takes the form

$$S_{\mu\nu}^{\alpha} \equiv \frac{\partial S_{\mu\nu}}{\partial \alpha} = \frac{\partial \langle \phi_{\mu} | \phi_{\nu} \rangle}{\partial \alpha} = \langle \chi_{\mu} | \chi_{\nu} \rangle, \quad (14)$$

$$h_{\mu\nu}^{\alpha} \equiv \frac{\partial h_{\mu\nu}}{\partial \alpha} = \langle \chi_{\mu} | V_N | \chi_{\nu} \rangle, \quad (15)$$

and

$$\begin{aligned} \langle \mu\kappa \| \nu\lambda \rangle^{\alpha} &\equiv \frac{\partial \langle \mu\kappa \| \nu\lambda \rangle}{\partial \alpha} \\ &= (\chi_{\mu} \chi_{\nu} | \phi_{\kappa} \phi_{\lambda}) + (\phi_{\mu} \phi_{\nu} | \chi_{\kappa} \chi_{\lambda}) \\ &\quad - (\chi_{\mu} \chi_{\lambda} | \phi_{\kappa} \phi_{\nu}) - (\phi_{\mu} \phi_{\lambda} | \chi_{\kappa} \chi_{\nu}), \end{aligned} \quad (16)$$

where

$$\chi_{\mu} = \frac{1}{2c} \boldsymbol{\sigma} \cdot \mathbf{p} \phi_{\mu}. \quad (17)$$

We note that the first derivative of the overlap matrix is nonzero (Sadlej et al.²⁰ also note that “[i]t should be pointed out that in the DPT approach based on the Lévy–Leblond equation both the Hamiltonian itself and the metric are involved, since both depend on the same parameter α ”). If analytical energy gradients are available for a given implementation of CC theory or MBPT, our recipe for implementing the computation of the first-order relativistic correction from DPT is the following: *feed the existing computer code for analytical energy gradients with the above derivatives of one- and two-electron integrals.*

This simple recipe is easily verified for HF theory. With the energy-weighted density matrix

$$W_{\mu\nu}^{(0)} = \sum_i \varepsilon_i^{(0)} [c_{\mu i}^{(0)}]^* c_{\nu i}^{(0)}, \quad (18)$$

the energy gradient of HF theory can be written as

$$\begin{aligned} E_{\text{HF}}^{(1)} \equiv \frac{\partial E_{\text{HF}}}{\partial \alpha} &= \sum_{\mu, \nu} P_{\mu\nu}^{(0)} \left[h_{\mu\nu}^{\alpha} + \frac{1}{2} \sum_{\kappa, \lambda} P_{\kappa\lambda}^{(0)} \langle \mu\kappa \| \nu\lambda \rangle^{\alpha} \right] \\ &\quad - \sum_{\mu, \nu} W_{\mu\nu}^{(0)} S_{\mu\nu}^{\alpha}. \end{aligned} \quad (19)$$

Inserting the derivatives of eqs. (14)–(17) leads to

$$\begin{aligned} E_{\text{HF}}^{(1)} &= \frac{1}{c^2} \sum_i \{ \langle \psi_i^{(0)} | V_N + J_{11}^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(0)} \rangle \\ &\quad - \langle \varphi_i^{(0)} | K_{12}^{(0)} | \psi_i^{(0)} \rangle \}, \end{aligned} \quad (20)$$

where

$$\begin{aligned} \langle \omega | J_{11}^{(0)} | \tau \rangle &= \sum_i (\varphi_i^{(0)} \varphi_i^{(0)} | \omega \tau), \\ \langle \omega | K_{12}^{(0)} | \tau \rangle &= \sum_i (\varphi_i^{(0)} \omega | \psi_i^{(0)} \tau). \end{aligned} \quad (21)$$

Equation (20) is equal to eq. (5.10b) of ref. 15, except for an obvious misprint in the latter.

The derivatives of eqs. (14)–(17) can be used directly to compute the first-order DPT correction to the MBPT or CC energy. The techniques for computing MBPT or CC energy gradients can be used with little or no modification. Furthermore, it is noteworthy that our recipe can also be followed for implementing the DPT correction in the framework of DFT as was very recently done by van Wüllen.¹⁹ For example, in the local density approximation (LDA) for a closed-shell system, the per-

turbation expansion of the exchange-correlation (XC) energy is given by

$$E_{\text{XC}} = \int F_{\text{XC}}(\rho^{(0)}) d\mathbf{r} + \alpha \int \left(\frac{\partial F_{\text{XC}}(\rho)}{\partial \rho} \frac{\partial \rho}{\partial \alpha} \right)_{\alpha=0} d\mathbf{r} + \dots, \quad (22)$$

where ρ is the electron density,

$$\rho = \sum_i (\varphi_i^* \varphi_i + \psi_i^* \psi_i). \quad (23)$$

Hence, it is obvious that the first-order DPT correction to the nonrelativistic LDA energy is obtained by changing the first derivative $h_{\mu\nu}^\alpha$ of eq. (15) to

$$h_{\mu\nu}^\alpha(\text{LDA}) = \langle \chi_\mu | V_N + V_{\text{XC}}^{(0)} | \chi_\nu \rangle, \quad (24)$$

where $V_{\text{XC}}^{(0)}$ is the XC potential computed from $\rho^{(0)}$,

$$V_{\text{XC}}^{(0)} = \left(\frac{\partial F_{\text{XC}}(\rho)}{\partial \rho} \right)_{\rho=\rho^{(0)}}, \quad \rho^{(0)} = \sum_i [\varphi_i^{(0)}]^* \varphi_i^{(0)} \quad (25)$$

(the fact that the zeroth-order XC potential $V_{\text{XC}}^{(0)}$ must be used in eq. (24) was not fully appreciated in ref. 19). We automatically obtain

$$E_{\text{LDA}}^{(1)} = \frac{1}{c^2} \sum_i \langle \psi_i^{(0)} | V_N + V_{\text{XC}}^{(0)} + J_{11}^{(0)} - \varepsilon_i^{(0)} | \psi_i^{(0)} \rangle \quad (26)$$

for the first-order DPT correction to the LDA energy if the appropriate derivatives of one- and two-electron integrals are inserted into the corresponding expression for the energy gradient.

In summarizing this section, we note that it is straightforward to implement the computation of the first-order DPT correction if analytical energy gradients are available for the method under consideration. Furthermore, the availability of analytical second derivatives for a given method will readily allow for the computation of the analytical gradient of the DPT correction itself, and thus allow for molecular geometry optimizations at the corresponding level of theory with the inclusion of relativistic effects in the framework of first-order DPT.

Computational Details

The calculations were performed with the DIRCCR12-95 program²¹ on IBM RS/6000 work-

stations at the ETH Zürich Computing Center. The program employs the HERMIT program²² to generate one- and two-electron integrals, for which first and second derivatives are available.

In the first order with respect to $1/c^2$, the DPT method gives essentially the first-order result of the Pauli approximation, where the MVD terms are added to the nonrelativistic Hamiltonian. For this approach, the derivatives

$$S_{\mu\nu}^\alpha = 0, \quad (27)$$

$$h_{\mu\nu}^\alpha = -\frac{1}{8c^2} \langle \phi_\mu | p^4 | \phi_\nu \rangle + \frac{\pi}{2c^2} \sum_A Z_A \langle \phi_\mu | \delta^3(\mathbf{r}_{1A}) | \phi_\nu \rangle, \quad (28)$$

and

$$\begin{aligned} & \langle \mu\kappa || \nu\lambda \rangle^\alpha \\ &= -\frac{\pi}{c^2} \left\{ \langle \phi_\mu(1) \phi_\kappa(2) | \delta^3(\mathbf{r}_{12}) | \phi_\nu(1) \phi_\lambda(2) \rangle \right. \\ & \quad \left. - \langle \phi_\mu(1) \phi_\kappa(2) | \delta^3(\mathbf{r}_{12}) | \phi_\lambda(1) \phi_\nu(2) \rangle \right\} \quad (29) \end{aligned}$$

are required. The one-electron MVD terms are available in most quantum chemistry programs, but the two-electron Darwin term is often not computed. However, the MVD results presented in the present work also include the two-electron Darwin term. The implementation of this term requires only a minor change to the HERMIT program, which is based on recurrence relations that start from the intermediate quantities

$$\begin{aligned} R_{000,m} &= (-2\gamma)^m F_m(W) \\ &= (-2\gamma)^m \int_0^1 t^{2m} \exp(-Wt^2) dt. \quad (30) \end{aligned}$$

These intermediates must be replaced by

$$R_{000,m}^\alpha = \frac{1}{4c^2} (-2\gamma)^{m+1} \exp(-W) \quad (31)$$

to obtain the two-electron Darwin integrals.

Analytical energy gradients are currently not at our disposal in the DIRCCR12-95 program. Therefore, the numerical results of the present work were computed by applying finite perturbation theory instead of being computed analytically. Gaussian basis sets were employed with both uncontracted²³⁻²⁶ and atomic natural orbital (ANO) contractions,²⁷⁻²⁹ and only the spherical harmonic

TABLE I.
First-Order Relativistic Correction (in E_h) to Ground State Energy of Closed-Shell Atoms.

Atom	Basis	Method	HF	MBPT(2)	CCSD	CCSD(T)
He	6s4p3d ^a	DPT	−0.000 133 01	−0.000 131 62	−0.000 133 24	
		MVD	−0.000 133 03	−0.000 131 55	−0.000 133 18	
Be	6s4p3d2f ^a	DPT	−0.002 867	−0.002 855	−0.002 849	−0.002 849
		MVD	−0.002 868	−0.002 852	−0.002 846	−0.002 845
Ne	6s5p3d2f ^a	DPT	−0.144 41	−0.144 56	−0.144 51	−0.144 53
		MVD	−0.144 59	−0.144 71	−0.144 66	−0.144 67
Ar	7s6p4d3f ^b	DPT	−1.850 49	−1.849 95	−1.849 88	−1.849 87
		MVD	−1.853 88	−1.853 15	−1.853 09	−1.853 08

Correction obtained from direct perturbation theory (DPT) and mass-velocity-Darwin (MVD) perturbation theory.

^aANO basis from ref. 27.

^bANO basis from ref. 28.

components of the basis functions were used. Moreover, the nuclei were point shaped and a numerical value of $c = 137.035\,989\,5$ au was used.

Preliminary Results

To test our new implementation of first-order DPT, we performed MBPT and CCSD(T) calculations on the closed-shell atoms He, Be, Ne, and Ar, employing both the DPT and MVD perturbations. Results obtained with generally contracted ANO basis sets^{27,28} are presented in Table I where the first-order energy $E^{(1)}$ is given. Considering the moderate size of the basis sets, the first-order DPT results from ref. 16 are nicely reproduced at the

HF level. It is also obvious that first-order DPT and MVD perturbation theory are very similar, although a noticeable basis set effect is observed for Ar. The AO basis set limit first-order DPT-CCSD value for He is $-0.000\,132\,1\,E_h$,^{17,18} which is $1.2\,\mu E_h$ above the respective HF value. However, the CCSD value obtained with the 6s4p3d basis is slightly *below* the HF result, because this basis fails to recover contributions of about $+1.3\,\mu E_h$ from basis functions of the f type and higher.^{17,18}

In Table II first-order DPT-MBPT results for Be, Ne, and Ar are compared with relativistic MBPT(2) and MBPT(3) contributions computed by Quiney et al.³⁰ and Ishikawa et al.^{24,25} For the purpose of an unambiguous comparison, we used the same

TABLE II.
MBPT Contributions (in μE_h) to First-Order Relativistic Correction to Ground State Energy of Closed-Shell Atoms.

Atom	Basis	Method	MBPT(2)	MBPT(3)	MBPT(4)	Reference
Be	14s ^a	DPT	−7.53	−1.99	−0.39	Present work
		MVD	−7.57	−1.99	−0.38	Present work
			−7.55	−1.98		Ishikawa et al. ²⁴
			−7.5			Quiney et al. ³⁰
Ne	14s10p8d6f ^b	DPT	−243	+44	−35	Present work
		MVD	−245	+45	−35	Present work
			−251	+44		Ishikawa et al. ^{24,25}
Ar	16s11p9d7f ^c	DPT	−996	+80	+2	Present work
		MVD	−1001	+80	+2	Present work
			−1080	+84		Ishikawa ²⁵

Results obtained from direct perturbation theory (DPT) and mass-velocity-Darwin (MVD) perturbation theory are compared with values from the literature.

^aUncontracted basis from ref. 26.

^bUncontracted basis from ref. 23.

^cUncontracted basis from ref. 25.

basis sets as in refs. 23–25. Excellent agreement was achieved for the MBPT(2) and MBPT(3) relativistic energies, as higher order effects of $O(c^{-4})$ can be expected to be very small for Be, Ne, and Ar. Furthermore, the difference between first-order DPT and MVD perturbation theory is found to be almost negligible with the large uncontracted basis sets.

The equilibrium bond distance of CuH was computed with a $7s6p4d3f2g/4s3p2d$ ANO basis set,^{27,29} and the results are presented in Table III. Excellent agreement with the DHF results obtained by Collins and colleagues⁵ is found at the HF level. The bond length contraction of 0.027 Å due to relativistic effects also agrees very well with the value of 0.026 Å computed by Collins et al.⁵ However, the DPT-MBPT(2) value of $r_e = 1.423$ Å is slightly shorter (by 0.009 Å) than the DHF-MBPT(2) bond distance,⁵ and the DPT-CCSD(T) value is too short by 0.009 Å in comparison with the experimental value.³¹ This disagreement is presumably due to a relatively large basis set superposition error (BSSE). Collins and coworkers⁵ reported a BSSE of about 0.01 Å in their calculations using a $7s6p5d2f/4s3p1d$ basis set, and a BSSE of the same order of magnitude is expected

in our calculations. Furthermore, the $3s/3p$ semicore orbitals of Cu were not correlated in the present work. Electron correlation effects due to correlating these orbitals shortened the Cu—H distance by 0.004 Å in the DHF-MBPT(2) calculations in ref. 5. These two effects, BSSE and $3s/3p$ semicore correlation effects, must be accounted for to obtain the accuracy achieved in the relativistic multireference CI calculations by Marian.³² Moreover, agreement between the nonrelativistic coupled-pair functional (CPF) results obtained by Chong et al.³³ and the present nonrelativistic MBPT(3) or CCSD results is satisfactory.

Table IV shows results^{34–38} for the tetrahedral SiH₄ molecule from two different ANO contractions.^{27,28} The equilibrium bond distance r_e was computed from a “small” $6s5p3d/2s1p$ and a “large” $7s6p4d3f/3s2p1d$ basis set (for Si/H). The computed bond distances are quite similar for both sets. With the large basis, the Si—H bond distance is about 0.0008–0.0016 Å shorter than with the small basis, and the basis set effect is most pronounced at the HF level. The relativistic bond length contraction from first-order DPT is largely the same for both sets. At the HF level, the contraction is ≈ 0.0008 Å, and at the CCSD(T)

TABLE III.
Equilibrium Bond Distance r_e (in Å) of CuH.

Method	7s6p4d3f2g / 4s3p2d Basis Set ^a		Literature
	NR ^b	DPT ^c	
HF	1.569	1.542	1.539, ^d 1.542, ^e 1.541 ^f
MBPT(2)	1.450	1.423	1.432 ^g
MBPT(3)	1.509	1.480	
MBPT(4)	1.447	1.422	
CCSD	1.493	1.464	
CCSD(T)	1.482	1.454	
			1.509 ^h
			1.466 ⁱ
Experiment			1.463 ^j

Distance obtained from first-order DPT applied to various electron correlation methods (correlating the 12 valence electrons).

^aANO basis set for Cu / H from refs. 27 and 29.

^bNonrelativistic result.

^cFirst-order relativistic DPT result.

^dPerturbative CG-HF result from ref. 5.

^eDouglas–Kroll–HF result from ref. 5.

^fDHF result from ref. 5.

^gDHF-MBPT(2) result from ref. 5.

^hNonrelativistic coupled-pair functional result from ref. 33.

ⁱRelativistic Douglas–Kroll multireference CI result from ref. 32.

^jRef. 31.

TABLE IV.
Equilibrium Bond Distance r_e (in Å) of Tetrahedral SiH.

Method	Basis Set ^a				Literature
	6s5p3d/2s1p		7s6p4d3f/3s2p1d		
	NR ^b	DPT ^c	NR ^b	DPT ^c	
HF	1.477 0	1.476 2	1.475 4	1.474 6	1.482, ^d 1.477 ^e 1.487, ^f 1.477 ^g
MBPT(2)	1.476 7	1.476 0	1.475 0	1.474 3	
MBPT(3)	1.477 7	1.477 0	1.476 7	1.476 0	
MBPT(4)	1.479 3	1.478 7	1.478 6	1.477 9	
CCSD	1.479 5	1.478 8	1.478 6	1.477 9	
CCSD(T)	1.480 5	1.479 9	1.479 7	1.479 0	1.460 ^h
Experiment					1.475 ⁱ

Distance obtained from first-order DPT applied to various electron correlation methods (correlating the eight valence electrons).
^aANO basis sets for Si/H from refs. 27 and 28.
^bNonrelativistic result.
^cFirst-order relativistic DPT result.
^dPerturbative CG-HF result from ref. 34.
^eDHF result from ref. 35.
^fDHF result from ref. 36.
^gCG based quasirelativistic model potential result from ref. 37.
^hNonrelativistic ECP/CCSD(T) result from ref. 38.
ⁱExperimental r_e as estimated in ref. 35.

level, it is ≈ 0.0007 Å. The DPT-HF contraction compares very well with the CG-HF value of 0.00084 Å reported by Dyall and cohorts.³⁵ These authors note, however, that there is a considerable difference (0.00018 Å) between the computed relativistic bond length contractions from the CG-HF and DHF approaches due to “spin-orbit and self-consistent effects.” Furthermore, we found noticeable discrepancies between the present results and those obtained by Visser et al.³⁶ as well as Hein et al.³⁸ The DHF bond distance computed by Visser et al.³⁶ is too short by ≈ 0.001 Å, and the ECP/CCSD(T) bond distance obtained by Hein et al.³⁸ is too short by ≈ 0.002 Å. These discrepancies are probably due to the rather small basis sets used by these authors,^{36,38} namely a 9s6p/3s basis (for the large component) and a basis set of “double-zeta plus polarization” quality, respectively. Our best DPT-CCSD(T) result was $r_e = 1.479$ Å, which is 0.004 Å longer than the “experimental” value as obtained by Dyall et al.³⁵ by estimating an appropriate correction to the experimental r_0 value.

Summary

Relativistic effects were computed for the closed-shell atoms He, Be, Ne, and Ar, and

molecules CuH and SiH₄ at the MBPT(4) and CCSD(T) levels of theory by means of first-order DPT. This theory is very similar to the first-order MVD perturbation theory and can be readily implemented into computer codes for nonrelativistic electron correlation methods.

The calculations of the present work did not account for spin-orbit effects. Furthermore, they were based on the Coulomb interaction, and effects due to the Breit interaction were not investigated.

First-order DPT calculations at the correlated level are not prohibitively expensive from a computational point of view and might become an interesting alternative to the established CG approach. At present, it seems most promising to study relativistic effects beyond the first order at the DPT-HF level and to compute the interplay between relativistic and correlation effects at the first-order of DPT applied to high-level electron correlation methods.

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